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## Atmospheric Oxygen Measurements and the Carbon Cycle

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## Abstract

Precise measurements of atmospheric  $O_2$  concentration can provide constraints on several aspects of the global carbon cycle. Seasonal variations in  $O_2$  concentration, driven in part by biological and physical cycles in the ocean, can be used to constrain seasonal net photosynthesis rates of marine biota. Interannual variations in  $O_2$  concentration, driven largely by  $O_2$  uptake by fossil fuel burning and  $O_2$  exchanges with land biota, can be used to partition the net global uptake of anthropogenic  $CO_2$  into oceanic and land biotic components. The latter application is potentially complicated, however, by interannual sources and sinks of  $O_2$  from the ocean. Model simulations are presented that suggest that interannually driven air-sea  $O_2$  exchanges may be several times larger on a mole-for-mole basis than interannually driven air-sea  $CO_2$  exchanges.

## 10.1 Introduction

It has recently become feasible to measure the atmospheric oxygen concentration to a degree of precision that allows for the detection of variations in the remote atmosphere (Keeling and Shertz, 1992; Bender et al., 1994; Bender et al., 1996; Keeling et al., 1996). These variations primarily reflect changes in  $O_2$  because  $N_2$  is constant to a very high level. Variations in  $O_2$  are caused primarily by production and consumption of  $O_2$  by photosynthesis, respiration, and combustion, and are thereby tied to the rate at which carbon is transformed between organic and inorganic forms. This link between  $O_2$  and organic carbon means that atmospheric oxygen measurements can be used to constrain the rates and patterns of ocean biological productivity and the distribution of the sink for anthropogenic  $CO_2$  between the land and the ocean.

Early results from samples collected at three sea-level sites – Alert, Ellesmere Island (82.5°N, 62.3°W); La Jolla, California (32.9°N, 117.3°W); and Cape Grim, Tasmania (40.7°S, 114.7°E) – were reported by Keeling and Shertz (1992) and are shown in Figure 10.1. Clearly detectable seasonal variations in oxygen concentration are evident at all three sites. An interannual decrease in  $O_2/N_2$  is clearly evident in the La Jolla data. Concurrent  $CO_2$  data are also given. Changes in  $O_2/N_2$  are reported as deviations in the  $O_2/N_2$  ratio relative to reference:

$$\delta (O_2/N_2) = \left( \frac{(O_2/N_2)_{\text{sample}}}{(O_2/N_2)_{\text{reference}}} \right) \quad (10.1)$$

The resulting deviations  $\delta (O_2/N_2)$  are multiplied by  $10^6$ , and the result is expressed in (“per meg”) units. In these units,  $1/0.2095 = 4.8$  per meg is equivalent to 1 ppmv because  $O_2$  comprises 20.95% of air by volume (Machta and Hughes, 1970). Additional measurements of atmosphere oxygen concentration have been reported more recently by Keeling and colleagues (1996), Bender and colleagues (1996), and Keeling and colleagues (1998).

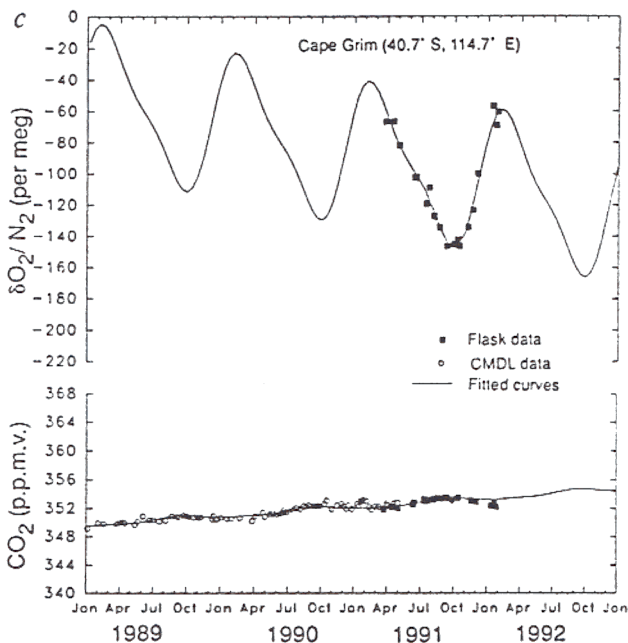
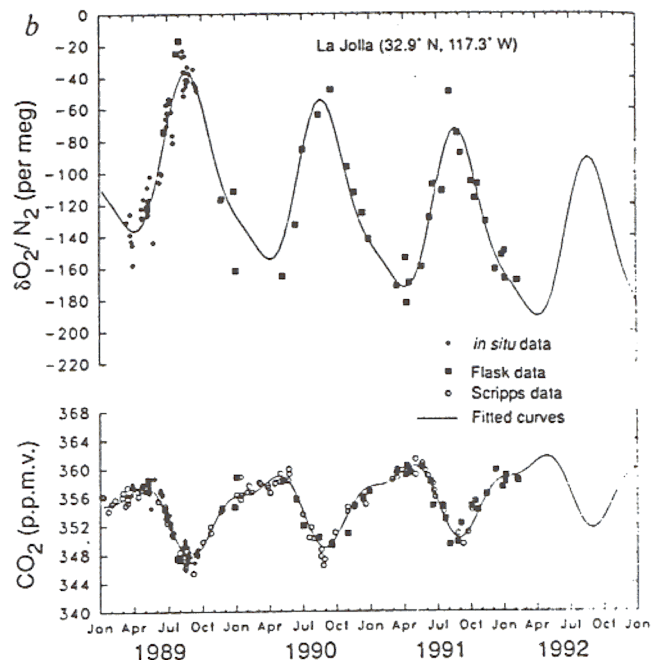
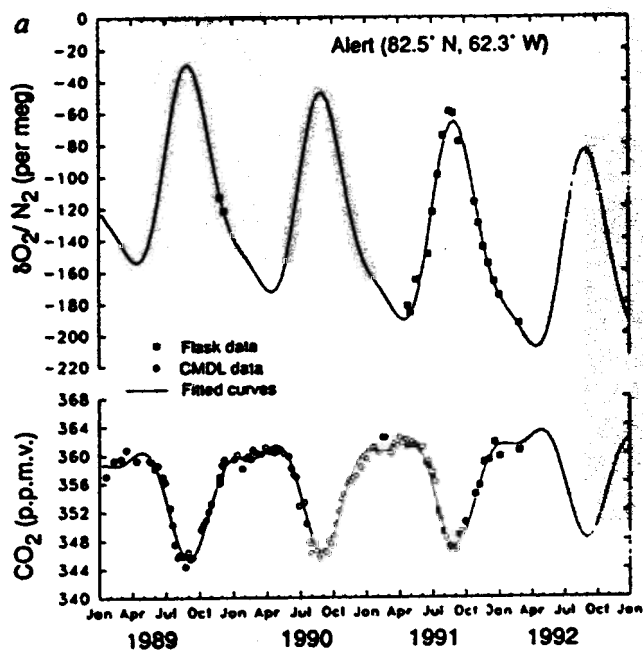
## 10.2 Seasonal Variations

The seasonal variations in oxygen concentration can be accounted for on the basis of three processes (Keeling and Shertz, 1992; Keeling et al., 1993). The first is the seasonal uptake and release of  $O_2$  resulting from photosynthesis and respiration of terrestrial ecosystems. These exchanges of  $O_2$  are closely tied to exchanges in  $CO_2$  with an  $O_2/CO_2$  exchange ratio of approximately  $-1.05:1$  (Keeling, 1988). The seasonal variations in  $CO_2$  in the Northern Hemisphere are almost entirely caused by these terrestrial exchanges, and they can be used to correct for the effects of terrestrial exchange on the  $O_2$  concentration variations. The residual variations in  $O_2$  concentration must be nonterrestrial, that is, oceanic, in origin. In the Southern Hemisphere, the lack of a large seasonal variation in  $CO_2$  indicates that the  $O_2$  concentration variations are almost entirely of oceanic origin.

The second process leading to seasonal variations is the warming and cooling of the upper oceans, which leads to seasonal ingassing and outgassing of  $O_2$  and  $N_2$  as determined by the solubility-temperature relations of these gases. Estimates of these exchanges based on seasonal changes in heat storage in the upper ocean suggest that this component of the seasonal variations is quite small, accounting for approximately 15% of the oceanic contribution to the seasonal variations in  $O_2$  ratio (Keeling and Shertz, 1992).

The third process is the seasonal variations in photosynthesis, respiration, and vertical mixing in the upper ocean. Generally, there is net production of  $O_2$  in the euphotic zone (approximately the upper 100 m of the ocean) where, on average, gross photosynthesis exceeds gross respiration, and there is a net consumption of  $O_2$  below the euphotic zone by respiration. Both the net  $O_2$  production rate in the euphotic zone and the rate of vertical mixing between the euphotic zone and deeper waters undergo large seasonal variations. At middle and high latitudes, the highest production rates tend to occur in the spring and summer when the waters above 100 m are well stratified (Peng et al., 1987; Asper et al., 1992). A considerable fraction of the  $O_2$  produced at this time escapes into the atmosphere. Comparable amounts of  $O_2$  are removed from the atmosphere in the fall and winter when stratification breaks down and oxygen-depleted waters from below 100 m depth are brought back into contact with the surface. The air-sea  $O_2$  fluxes associated with this seasonal cycle are linked to the rate at which organic material is produced and exported from the euphotic zone (Jenkins and Goldman, 1985; Keeling et al., 1993), and they are linked to changes in dissolved inorganic carbon (DIC) in the water. The seasonal air-sea fluxes of  $CO_2$  associated with these changes are much smaller than the  $O_2$  fluxes because most of the dissolved inorganic carbon is in the form of carbonate and bicarbonate ions, which are not exchanged across the air-sea interface.

The marine biological component of the seasonal variations can be used to constrain estimates of the annual net photosynthetic production of organic carbon in the euphotic zone if  $O_2$  transport within the atmosphere and between the euphotic zone of the oceans and the deeper waters is taken into account.



**Figure 10.1:** Measurements of  $\delta(\text{O}_2/\text{N}_2)$  and  $\text{CO}_2$  mole fraction at (a) Alert, (b) La Jolla, and (c) Cape Grim from the oxygen program directed by R. Keeling, now at Scripps Institution of Oceanography in La Jolla, California and formerly of the National Center for Atmospheric Research in Boulder, Colorado. The axes are scaled ( $5 \text{ per meg} \propto 1 \text{ ppm}$ ) so that changes in  $\delta(\text{O}_2/\text{N}_2)$  and  $\text{CO}_2$  are directly comparable on a mole  $\text{O}_2$  to mole  $\text{CO}_2$  basis. The data are shown against curve fits based on the sum of a four-harmonic seasonal function and a stiff-spline interannual trend, where the spline stiffness is adjusted to suppress frequencies higher than about 1 year. Reprinted with permission from *Nature*. R. F. Keeling and S. R. Shertz, *Nature* 358:723–27, © 1992, MacMillan Magazines Limited.

Using preliminary estimates of these quantities combined with the data shown in Figure 10.1, and assuming a Redfield ratio of 1.4:1 for  $\text{O}_2/\text{C}$  in marine organic matter, Keeling and Shertz (1992) estimated the global rate of net euphotic zone production to be 19 Gt C/yr.

Measurements of seasonal variations in  $\text{O}_2/\text{N}_2$  spanning many years could provide an index of interannual variations in marine productivity on large spatial scales. Such data would be valuable for monitoring the sensitivity of marine productivity to climate change, decreasing stratospheric ozone, eutrophication, or other perturbations.

### 10.3 Long-Term Oxygen Depletion

It has long been noted that there is a mismatch between the combined sources of  $\text{CO}_2$  from fossil fuel burning and land-use changes and the combined sinks in the ocean and the atmosphere. An additional missing sink for carbon is needed to balance things out (Keeling et al., 1989; Tans et al., 1990). This missing sink is of the same order of magnitude as the annual increase in atmospheric  $\text{CO}_2$ ; consequently, identifying this sink is clearly important for estimating future  $\text{CO}_2$  increases.

The most likely possibility for this sink is some sort of undocumented uptake of CO<sub>2</sub> by the land biosphere. At present, however, we cannot rule out the possibility that the oceans might be taking up more CO<sub>2</sub> than current models allow. This question of whether the missing sink is on land or in the ocean, or some combination of both, would be resolved if we could directly determine the net uptake of CO<sub>2</sub> by the oceans or the land biosphere. One method of obtaining this information involves using measurements of the long-term trend in atmospheric O<sub>2</sub>.

Over the long term, we can represent the global budget for atmospheric CO<sub>2</sub> according to

$$\Delta\text{CO}_2 = F + C - O + B \quad (10.2)$$

where  $\Delta\text{CO}_2$  is the annual averaged change in atmospheric CO<sub>2</sub>,  $F$  is the source of CO<sub>2</sub> from burning fossil fuels,  $C$  is the CO<sub>2</sub> source from cement manufacturing,  $O$  is the oceanic CO<sub>2</sub> sink, and  $B$  is the net source of CO<sub>2</sub> from terrestrial ecosystems ( $B$  can be positive or negative), all in units of mol/yr. Likewise, we can represent the budget for atmospheric oxygen according to

$$\Delta\text{O}_2 = -F - H - \alpha_B B \quad (10.3)$$

where  $\Delta\text{O}_2$  is the change in atmospheric oxygen,  $H$  is the O<sub>2</sub> sink owing to the oxidation of hydrogen and other elements besides carbon in fossil fuels, and  $\alpha_B$  represents the O<sub>2</sub>/C exchange ratio for terrestrial biomatter. There is no term in the long-term O<sub>2</sub> budget corresponding to the oceanic term in the CO<sub>2</sub> budget. This is because oceanic uptake of CO<sub>2</sub> essentially proceeds through reaction between dissolved CO<sub>2</sub> and carbonate ions, and therefore does not involve O<sub>2</sub>. Also, the oceans do not significantly buffer the decrease in atmospheric O<sub>2</sub> because the amount of O<sub>2</sub> dissolved in the oceans is less than 1% of the amount in the atmosphere.

Adding Equations (10.2) and (10.3) and solving for  $O$  yields

$$O = -(\Delta\text{O}_2 + H) - (\Delta\text{CO}_2 - C) - (\alpha_B - 1)B \quad (10.4)$$

The last term on the right-hand side of Equation (10.4) can be evaluated by solving Equation (10.3) for  $B$ , although this term is small, since  $\alpha_B \approx 1$ . Solving Equation (10.3) for  $B$  yields

$$B = -(1/\alpha_B)(\Delta\text{O}_2 + F + H) \quad (10.5)$$

These equations show how observations of the change in atmospheric O<sub>2</sub> combined with estimates of fossil fuel CO<sub>2</sub> production and O<sub>2</sub> consumption can be used to directly calculate the net exchange of CO<sub>2</sub> with the oceans and with the land biosphere.

Using measurements of the O<sub>2</sub> and CO<sub>2</sub> trends from 1991 to 1994, Keeling and colleagues (1996) derive an estimate of global oceanic uptake of  $1.7 \pm 0.9$  Gt C/yr and a net terrestrial carbon sink of  $2.0 \pm 0.9$  Gt C/yr for 1991–94. The primary source of uncertainty comes from uncertainty in the O<sub>2</sub> trend, and this will decrease as longer records are obtained.

Assuming that the O<sub>2</sub> trend were measured sufficiently accurately, what would then limit our ability to resolve terrestrial and oceanic carbon fluxes using O<sub>2</sub> measurements? One limi-

tation arises because Equations (10.4) and (10.5) are both subject to uncertainty in the fossil fuel terms  $F$  and  $H$ . These quantities are estimated using statistics compiled by the United Nations for the production of different fuel categories (solids, liquids, gases), estimates of the fraction of each category oxidized, and estimates of the average elemental composition of the different fuel categories (Marland and Boden, 1991; Keeling, 1988). This approach leads to estimates of  $F + H = 6.86 \times 10^{14}$  mol/yr and  $H = 2.01 \times 10^{14}$  mol/yr for the year 1989. The errors in  $F + H$  are estimated to lie between 6% and 10%, and the error in  $H$  to lie between 8% and 14%, depending on whether the errors for different fuel categories are assumed to be correlated (high estimate) or uncorrelated (low estimate) (Keeling, 1988). These error estimates are actually only rough guesses. Taking these figures, the uncertainty in  $F + H$  alone contributes to an uncertainty of  $\pm 4.0 \times 10^{13}$  to  $\pm 7.0 \times 10^{13}$  mol/yr (0.5–0.8 Gt C/yr) in the net CO<sub>2</sub> source derived from Equation (10.5) and the uncertainty in  $H$  alone contributes to an uncertainty of  $\pm 1.6 \times 10^{13}$  to  $\pm 2.9 \times 10^{13}$  mol/yr (0.2–0.3 Gt C/yr) in the net CO<sub>2</sub> sink into the ocean derived from Equation (10.4).

It appears, therefore, that uncertainty in fossil fuel production ultimately limits the accuracy of determining the net terrestrial carbon source to approximately  $\pm 0.5$ – $\pm 0.8$  Gt C/yr using the oxygen trend as displayed in Equation (10.5). Although this estimate is perhaps not as accurate as one would like, it is still much more accurate than current estimates of the net CO<sub>2</sub> source based on land-use changes (Houghton, 1991; Houghton et al., 1987); consequently, O<sub>2</sub> measurements indeed have the potential to contribute significantly to our understanding of terrestrial carbon exchanges. Even more valuable, perhaps, is the possibility of constraining the net oceanic uptake of CO<sub>2</sub> to the level of  $\pm 0.3$  Gt C/yr using Equation (10.4). If the current model estimates of the uptake of CO<sub>2</sub> by the oceans could be validated to this level, this would strengthen the case that the missing CO<sub>2</sub> sink is on land.

#### 10.4 Interannual Variability

A limitation on the use of O<sub>2</sub> data to constrain terrestrial and oceanic carbon sources and sinks is uncertainty in the exchanges of O<sub>2</sub> between the oceans and the atmosphere on direct interannual time scales. Although uptake of anthropogenic CO<sub>2</sub> by the oceans has no effect on atmospheric O<sub>2</sub>, it is still possible that variability in ocean dynamics or biological activity could lead to interannual air–sea exchange of O<sub>2</sub>. Even a relatively small imbalance between the seasonal ingassing and outgassing fluxes of O<sub>2</sub> across the air–sea interface could lead to such variability. Equations (10.3) to (10.5) totally ignore any possible effects of the oceans on atmospheric O<sub>2</sub>, so we must either find another way to estimate air–sea exchanges of O<sub>2</sub> or be able to argue that these exchanges are very small.

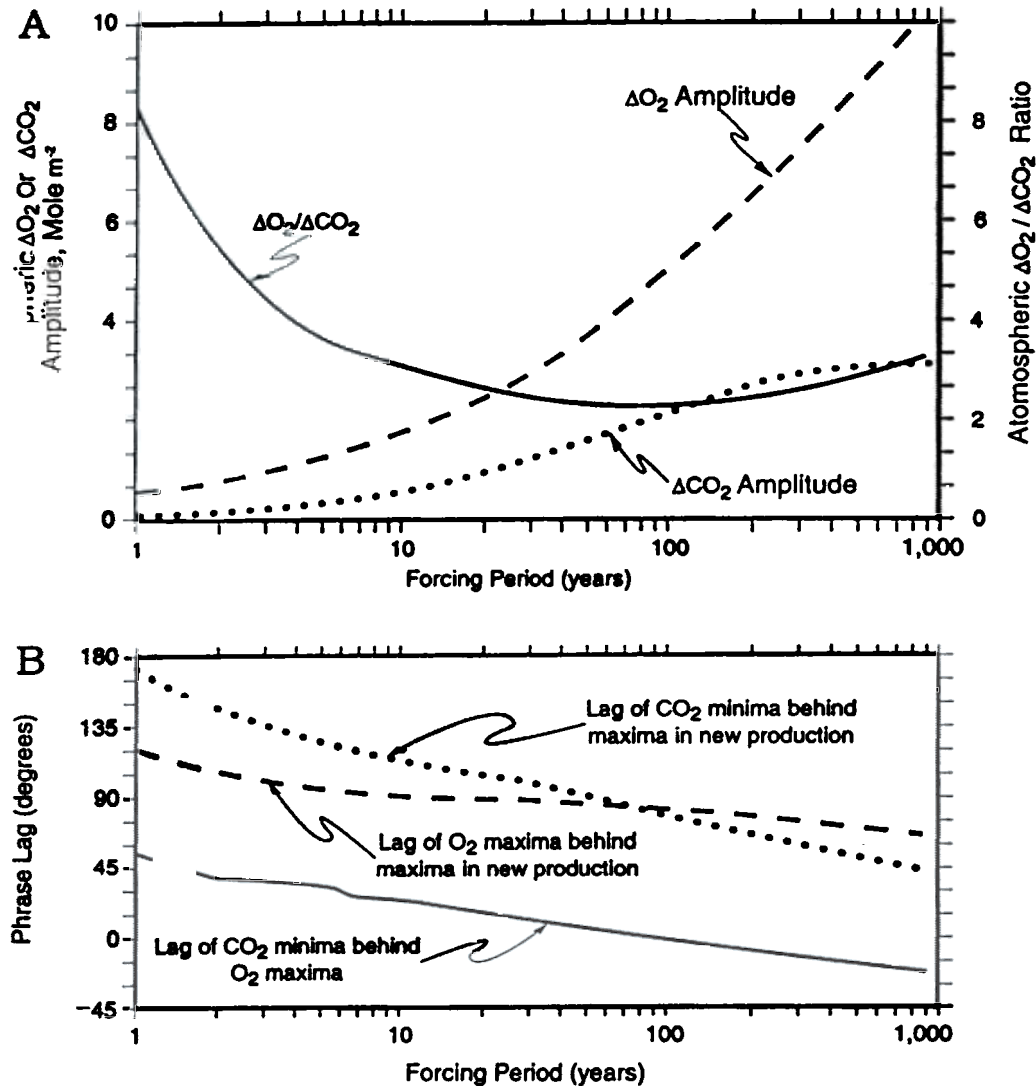
We have simulated the effects of interannual variability in biological productivity in the oceans using the high-latitude exchange/inferior diffusion-advection (HILDA) model (Joos et al., 1991; Shaffer and Sarmiento, 1995) coupled with a one-

box model of the atmosphere. The purpose of this simulation is to explore the link between  $O_2$  and  $CO_2$  variations in the air arising from variations in oceanic productivity. We force the biological new production in the model to vary sinusoidally in time, and we calculate the variations in dissolved  $O_2$  and dissolved inorganic carbon (DIC) in the ocean and variations in  $O_2$  and  $CO_2$  in the air arising from air-sea gas exchange. We express the results in terms of the amplitude ratio  $\Delta O_2/\Delta CO_2$  (mol/mol) of the variations in the air and in terms of the phase differences between the atmospheric  $O_2$  and  $CO_2$  variations. These quantities are not sensitive to the magnitude of the imposed variations in new production; however, they are sensitive to periodicity of the forcing. Figure 10.2 shows the sensi-

tivity of these quantities to variations in new production with periods ranging from 1 year to 1,000 years.

These simulations use a fixed Redfield  $O_2/C$  ratio of 1.43:1 for photosynthesis and respiration in the oceans. If  $O_2$  and  $CO_2$  partitioned themselves identically between the atmosphere and oceans, then the changes in atmospheric  $O_2$  and  $CO_2$  would occur in this ratio. In fact, this ratio is not obtained in the atmosphere at any time scale. The reason involves differences in the kinetics of gas exchange for  $O_2$  and  $CO_2$  and differences in the equilibrium chemical capacity of seawater to absorb excess  $O_2$  and  $CO_2$ .

When new production is forced with a period of one year, the atmospheric  $\Delta O_2/\Delta CO_2$  ratio is 8 (see Figure 10.2). Such a high



**Figure 10.2:** The effects of variable ocean productivity on atmospheric  $O_2$  and  $CO_2$ . (A) Peak-to-peak variations in  $\Delta O_2/\Delta CO_2$  and the  $\Delta O_2/\Delta CO_2$  ratio; and (B) relative phasing of the atmospheric  $O_2$  and  $CO_2$  variations. The results were simulated using HILDA ocean model coupled to a well-mixed atmospheric reservoir. In this application of the HILDA model, the mixing in the low-latitude box was set using CFC data ( $k = 465 + 7096e^{-0.220}$  in  $m^2/yr$ ). The model was modified by changing the ratio of  $CaCO_3$  to organic C production to 0.10 and adopting a remineralization scale of 800 m for organic particles and 500 m for  $CaCO_3$ . All other model parameters were used in Siegenthaler and Joos (1992). The new production in the model was varied sinusoidally between zero and twice the mean value. The mean new production was initially set at 1.3 mol  $C/m^2/yr$  for forcing with a period of one year. The mean was decreased as the square root of the period as the period was increased. This was done to prevent nutrients from being depleted in the upper boxes and to prevent anoxia from developing in the deeper waters.

ratio can be expected for seasonal variations (Keeling et al., 1993) because exchange of  $\text{CO}_2$  is heavily suppressed on this short time scale. Exchange of  $\text{CO}_2$  is slow because most DIC is in the form of carbonate and bicarbonate ions, which are not exchanged across the air-sea interface. As the period of the forcing is increased from 1 year to 80 years, the  $\Delta\text{O}_2/\Delta\text{CO}_2$  ratio decreases because  $\text{CO}_2$  now has more time to equilibrate with the atmosphere. The  $\Delta\text{O}_2/\Delta\text{CO}_2$  ratio achieves a minimum of approximately 2.2 at a period of 80 years and then increases for forcing with longer periods. This minimum ratio is still much larger than the Redfield ratio used. This minimum is probably quite sensitive to the remineralization depth range for organic matter and the mixing rates used in the model. A more realistic ocean model might produce lower  $\Delta\text{O}_2/\Delta\text{CO}_2$  ratios in the air (Sarmiento and Orr, 1991). Beyond 80 years, the  $\Delta\text{O}_2/\Delta\text{CO}_2$  ratio increases because perturbations in  $\text{CO}_2$  in the upper ocean have time to communicate with the deep sea, which has a large capacity for buffering atmospheric  $\text{CO}_2$  changes.

The possibility that there are net annual fluxes of  $\text{O}_2$  between the ocean and atmosphere may be especially relevant on the two- to five-year time scale on which El Niños occur. There is evidence that atmospheric  $\text{CO}_2$  is modulated at the ppm level on these time scales by the oceans (Whorf et al., 1993; Keeling et al., 1996). To the extent that these variations are related to variations in ocean biological productivity, we may expect, based on the above model simulations, that atmospheric  $\text{O}_2$  may vary by an amount 3 to 4 times larger. If such large fluxes of  $\text{O}_2$  do indeed occur, then we are likely to have serious difficulty in applying Equations (10.4) and (10.5) on this two- to five-year time scale. On the other hand, the atmospheric  $\text{O}_2$  variations would still impose valuable constraints on any such changes.

Variability in biology or circulation may also produce variability in atmospheric  $\text{O}_2$  on time scales longer than 5 years, although currently we have very little information that can be used to estimate the magnitude of such changes. In simulations that invoke relatively drastic alterations in oceanic productivity, Sarmiento and Orr (1991) found that although large air-sea fluxes of  $\text{CO}_2$  and  $\text{O}_2$  are possible on short time frames, the fluxes decrease significantly after approximately 10 years. High fluxes cannot be sustained over the long term because the  $\text{O}_2$  deficit or C excess of the water transported to the surface eventually adjusts itself to cancel out the effect of changing productivity.

To close the gap in the atmospheric  $\text{O}_2$  budget in decadal time scales, it may be necessary to develop independent constraints on decadal air-sea  $\text{O}_2$  exchanges. One approach would be to conduct surveys of the concentrations of preformed nutrients – that is, those nutrients that originated with the water masses when they left the surface – since any change in atmospheric  $\text{O}_2$  by marine biota must be accompanied by changes in the preformed nutrient distribution in the ocean (Keeling et al., 1993).

## 10.5 Summary

Measurements of the atmospheric  $\text{O}_2$  concentration can be applied to improve our understanding of the global carbon cycle.

One application uses the seasonal cycles in  $\text{O}_2$  concentration to impose constraints on estimates of marine biological productivities. Another application uses the long-term decrease in  $\text{O}_2$  concentration to constrain terrestrial and oceanic sources and sinks of  $\text{CO}_2$ . The latter application may be complicated by interannual sources and sinks of  $\text{O}_2$  from the oceans. To address this complication, it may be necessary to complement atmospheric  $\text{O}_2$  measurements with independent constraints on long-term exchanges of  $\text{O}_2$  between the atmosphere and the oceans.

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